-Comment-Draft

Meeting Minutes Transmittal/Approval Unit Manager's Meeting: 200-BP-1 Operable Unit 450 Hills Street, Richland, WA May 28, 1992

APPROVAL:	Allan Maria Date 6-25-92 Allan Harris, 200-BP-1 Unit Manager, RL (A5-19)
APPROVAL:	Date Doug Sherwood, 200ABP-1 Unit Manager, EPA (B5-01)
APPROVAL:	Darci Teel, 200-BP-1 Unit Manager, WA Department of Ecology
Meeting Minut	es are attached. Minutes are comprised of the following:
Attachm Attachm Attachm Attachm Attachm Attachm Attachm Attachm	ent #2 - Agenda for the Meeting ent #3 - Attendance List ent #4 - Status of Action Items ent #5 - Engineering Data Transmittal 158686 ent #6 - Approved Document Change Control Form No. 22 ent #7 - Outline of Risk Assessment Modeling ent #8 - Task 6 Activities ent #9 - Sorption/Column Leach Testing ent #10 - Sample Validation Summary ent #11 - Source and Vadose Sampling
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Prepared by:	Suzanne Clarke, GSSC Date: 6/25/92

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Attachment #1

Meeting Summary and Summary of Commitments and Agreements
Unit Manager's Meeting: 200-BP-1 Operable Unit
May 28, 1992

1. SIGNING OF THE APRIL 200-BP-1 MEETING MINUTES:

Minutes from the April 200-BP-1 Unit Manager's Meeting were reviewed and approved with no changes.

2. ACTION ITEM UPDATE: (See Attachment 4 for status)

2BP.51 Closed. (Item reported as 2BP.52 in April minutes.)

3. NEW ACTION ITEMS (INITIATED MAY 28, 1992):

2BP.53 Provide format for the sample validation summary information M. Buckmaster and the analyte data for the first three quarters of groundwater sampling to justify reducing the analyte list.

2BP.54 Provide summary table of results of near surface sampling to M. Buckmaster justify deletion of sampling points.

- 4. STATUS OF REMEDIAL INVESTIGATION TASKS:
 - <u>Risk Assessment Modeling:</u> Len Collard presented groundwater modeling for a hypothetical crib. See Attachment #7. The goal is to use actual data to refine the conceptual model.
 - O Doug Sherwood (EPA) requested 1) 60 Co and FeCN complexed metals have a K_d of 0; 2) WHC to look at the hydrologic properties of the four stratigraphic units used in the model; 3) historic groundwater table maps be evaluated as they may give information concerning historic groundwater mounding; 4) tables showing analytical data (in the same format as the Work Plan) for the first three quarters of groundwater sampling (Action Item 2BP.53).
 - Task 6, Phase IB Wells/Well Remediation: Complete. See Attachment #8.
 - Column Leach Testing: See Attachment #9.
 - Sample Validation Summary: See Attachment #10 and Action Item 2BP.53.
 - Source and Vadose Sampling: Complete. See Attachment #11.
- 5. SCHEDULE: On schedule for March 1993. See Attachment #12.

200-BP-1 UNIT MANAGERS MEETING AGENDA MAY 28, 1992 10:00-11:30 PM 450 HILLS ST., ROOM 47

	Introduction:	
	Status:	
	Action 1	tems:
	0	Borehole Reduction
_	Remedial	Investigation:
in	0	Risk Assessment Modeling
~	0	Task 6 Phase IB Wells/Well Remediation
CM499048	0	Column Leach/Sorption Testing
6	0	Chemical Data Status
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<i>∾</i>	Issues:	
•	Other To	ppics:
N	0	Schedule

Agreements and Commitments:

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200-BP-1 Operable Unit Manager's Meeting Official Attendance Record May 28, 1992

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Please print clearly and use black ink PRINTED NAME	SIGNATURE	ORGANIZATION	O.U. ROLE	TELEPHONE
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ACTION ITEMS

Item Number	Action	Status
2BP.51	Prepare a work plan change request to eliminate the 3, Task 2 background boreholes. Action: Buckmaster	Closed

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5. Key Words	6. Author	-	<u> </u>
Sorption properties, contaminants, minerals	Name: M. A. Bud	ckmaste	er
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SUMMARY

At the request of J. F. Relyea a literature search was performed to determine available data that describe the sorption properties of the following contaminants in Hanford Site soil: tritium, cesium, strontium, cobalt, bismuth, uranium, plutonium, cyanide, and phosphate. When available, Hanford Site-specific literature (i.e., data determined using Hanford soil) was reviewed to the exclusion of the general literature. Hanford-specific data were available for all of the listed contaminants except bismuth, cyanide, and phosphate. The general features of Hanford sediments include having a high sand content (\approx 70 to 80 wt%), being moderate in silt content (\approx 10 to 20 wt%), and low in clay content (<1 to 10 wt%). Predominant minerals in Hanford sediments include quartz, feldspar, and pyroxene with small amounts of calcium carbonate, micas, smectite clays, oxides, and apatites.

Table I summarizes our estimates for probable K_d (concentration in soil/concentration in solution, mL/g) values under ambient conditions, a plausible range of K_d values for ambient conditions, a descriptive quality factor and probable K_d ranges for chemical environments in soils dominated by two process waste-streams. These two environments are high ionic strength alkaline process water and high acid/high organic complexant process water. To calculate the retardation factor (R), it is necessary to know the bulk density of soil and water content (or porosity for a saturated soil) of the material of interest (the values of these variables must be determined or otherwise supplied by the user). The retardation factor is calculated as R = $1 + K_d \rho_b/\Theta$, where ρ_b is the bulk density and Θ is the water content (Bouwer, 1991).

Based on the results of this review, it is recommended that Hanford Site-specific adsorption data be determined for bismuth because its adsorption behavior is not well known. Further work is warranted for plutonium because its adsorption behavior in ambient Hanford conditions is not well known; however, it is known to be relatively immobile in most soil and groundwater environments studied. Determination of Hanford Site-specific data for cyanide and phosphate might deserve work, but it is known from the general literature that cyanide is poorly adsorbed to soils and the mobility of phosphate tends to be solubility controlled.

TABLE 1. Summary of K Data Specific to Hanford.

	Amb	ient Conditions	High Ionic Strength, Alkaline	High Acid/ Organic	
Species	Probable K _d (mL/g)	Range in K _d (mL/g)	Quality of Data ^(a)	Range in K _d (mL/g)	Range in K _d (mL/g)
³H(HTO)	0.0	0.0	1	0.0	0.0
¹³⁷ Cs ⁺	500	500-10,000	2	1-200	1-200
⁹⁰ Sr ²⁺	20	5-100	2	0.3-20	0-20
⁶⁰ Co ²⁺	2000	1000-10,000	2	200-2000	10-200
Bi ³⁺	1000	500-19,000	4	unknown	unknown
UO ₂ +	I	0-3	3	0-500	unknown
Pu ^(b)	100	100-2000	3	100-2000	1-100
⁹⁹ Tc0 ₄	. 0	0-1	2	0-1	0-1
HCN	0.1	unknown	4	unknown	unknown
HPO ₄ -	50	20-100	3	20-100	0-10

^(a) Quality Rating

- (1) K_d values are very well known, little chance for variation because of chemical changes.
- (2) K_d values are well known, variability caused by competing salts, pH, Eh and organics generally understood.
- (3) K_d values are fairly well known, variability caused by chemical factors (competing salts, redox, organics, etc.) not well documented.
- (4) K_d values are not known, probable value is purely an educated guess.
- The Pu oxidation state was not characterized and many forms can co-exist for Hanford ambient conditions $PuO_2^+ > PuO_2^{2+} > Pu^{4+} > Pu^{3+}$ is likely. Most waste streams at the Hanford Site would produce soluble Pu species with $PuO_2^+ + PuO_2^{2+} > Pu^{4+} + Pu^{3+}$. Some organic-rich Hanford waste streams could solubilize Pu^{4+} species.

ADSORPTION

Adsorption of dissolved contaminants onto solid surfaces is a process that is affected by a variety of other chemical reactions or processes including:

1) adsorption site density per unit area of adsorbent; 2) binding site strength, or affinity, of the adsorbate-adsorbent pair; 3) total amount of dissolved adsorbate available for interaction with the adsorbent surface; 4) speciation of the adsorbent (oxidation state and complexation state), for example, how strongly plutonium adsorbs will depend on if it is in the form of PuO_2^{2+} , Pu^{4+} , or $PuCO_3^{2+}$, etc.; and 5) the concentrations of competitive adsorbates.

Because K_d measurements are empirical values determined under a certain set of chemical conditions, they are only applicable to systems in which the chemical variables are the same as those used to determine the measured value, unless changes in a particular variable do not affect adsorption. In addition to the effects described in the previous paragraph, experimental artifacts can result in incorrect K_d values. The two most important of these potential problems results from precipitation of highly insoluble materials, which can bias K_d values high, and adsorption by "nonsettling" colloids, which can remain suspended in the aqueous phase after centrifugation or filtration in batch experiments or travel through the pores in column experiments (this effect will bias K_d values low).

Due to these considerations, it is necessary to have a firm understanding of the chemical systems from which the $K_{\rm d}$ values were determined and to which they are to be applied. Errors resulting from a lack of understanding of these systems can seriously compromise the quality of the data and the results of contaminant transport models. Adsorption data for the individual contaminants are reviewed in the following sections.

Tritium

Tritium (³H or T) is a radioactive isotope of hydrogen with a half-life of 12.3 years. Tritium is rapidly oxidized to HTO, which behaves essentially the same as ordinary water in terms of its transport properties. This means that tritium will travel at approximately the same velocity as soil water or

groundwater. Some exchange of tritiated water for regular water on clays and other hydrated soil constituents does occur, but this effect will not retard tritium migration to any significant extent. As a result we would expect tritium to have a K_d value of practically zero and a retardation factor (R) close to one. These expectations have been confirmed by both laboratory column and field studies conducted with Hanford soil or at the Hanford site (Brown and Haney, 1964; Brown, 1967; Haney et al., 1962; Haney, 1963, 1964; Wierenga et al., 1986). Recent laboratory column results also indicate that Hanford soils do not adsorb tritium.

The quality of our expected $K_{\rm d}$ value of 0.0 for tritium is considered very good because both field and laboratory column results conducted by independent researchers using Hanford Site-specific material confirm this expected value.

Cesium

Several investigations of cesium behavior in Hanford soil have been completed. Thermodynamic data summarized by Ames and Rai (1978) indicate that cesium will exist as a monovalent cation throughout the potential range of groundwater pH at Hanford. Cesium exhibits no tendency to complex with inorganic or organic ligands, to polymerize, or to form colloids. Consequently, Cs is expected to sorb primarily by ion exchange. The degree of sorption in Hanford soil is dependent on the types and concentrations of other cations in solution that can compete with cesium for sorption sites. The data indicate that all common cations (e.g., hydrogen, potassium, sodium, calcium, and magnesium) can influence cesium sorption depending on their concentrations. Experiments performed with Hanford soil are described below.

Rhodes and Nelson (1957) measured cesium K_d values as a function of pH. The hydrogen ion competition for sorption sites was greatest at pH values of 0.4 to 1.8, with Cs K_d values ranging from 37 and 138 mL/g, respectively. For pH values of 3 to 10, the measured Cs K_d values exceeded 200 mL/g. Routson et al. (1981) investigated the effects of varying the concentrations of potassium, sodium, and calcium on cesium sorption. Of these, potassium was

¹⁹⁹² unpublished results. Pacific Northwest Laboratory, Richland, Washington.

the most successful competitor, followed by sodium and calcium. Cesium K, values dropped from 280 to 5.8 mL/g as potassium concentrations increased from 10^{-3} to 2 x 10^{-1} M, respectively. In the presence of sodium, Cs $\rm K_d$ values were measured at >1200 mL/g for 1 \times 10⁻³ M sodium and then dropped to 570 mL/g at 1 x 10^{-3} M Na and to 26 mL/g at 3 M Na concentration. Calcium was the least influential competing cation with Cs K_d values decreasing only slightly (2200 to 790 mL/g) when Ca increased from 2 \times 10⁻³ to 2 \times 10⁻¹ M. Similarly, Barney (1978) measured cesium $K_{\rm d}$ in mixed cation systems composed of sodium and potassium with small amounts of humic acid (17 and 33 mg/L); the maximum potassium and sodium concentrations used were 10^{-2} and 1 x 10^{-1} M, respectively. All measured Cs K_d values exceeded 200 mL/g. Rhodes and Nelson (1957) also measured cesium K_d at much higher sodium concentrations (1 to 6 M) and observed significant decreases in Cs $K_{\rm d}$ (from 100 to 18 mL/g) as sodium concentrations increased. Ames and Rai (1978) report work on cesium sorption in simulated tank waste with competing cations (sodium, potassium, calcium, and ammonium) at combined concentrations of >2 M; they reported Cs ${\rm K_d}$ values from <1 to 14 mL/g.

In more recent work by Serne et al. (1991) distribution coefficients between Hanford Trench 8 sediment (from 200 W Area) and Hanford groundwater were measured. The Cs K_d after 5 days of contact was 540 \pm 30 and 690 \pm 80 after 44 days of contact. Earlier work by Serne et al. (1990) using Hanford sediment (CGS-1, W of 200 E Area; TBS-1, S of 200 W Area) resulted in much higher K_d values, which were dependent upon equilibration period. The CGS-1 data were 1270 \pm 36 at 4 days, 2190 \pm 414 at 14 days and 3120 \pm 630 at 35 days. The TBS-1 data were 3720 \pm 760 at 4 days, 5110 \pm 690 at 14 days and 14,000 \pm 1630 at 35 days. The differences between the earlier work and the more recent work appear to be related to differences in the concentration of Cs used in the experiments and/or differences in soil material (Trench 8 material contained 90.3% fines, CGS-1 soil contained 17.5 % fines and TBS-1 contained \approx 99 % fines).

Relatively little work has been completed to investigate the potential for cesium complexation with anionic ligands. However, data indicate that cesium does not interact with any common inorganic anions and has little interaction with most organic anions. Knoll (1969) observed that a small amount of sorbed

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cesium on a Hanford soil column (\approx 12% after 70 column volumes) could be desorbed when exposed to a flushing solution containing 0.4 M d-2-EHPA - 0.2 M TBP.

Given these data, sorption K_d values for cesium in Hanford soil will fall between 500 and >10,000 mL/g. Under ambient conditions [i.e., near neutral in pH, relatively low ionic strength (\approx 1 x 10^{-3} M for competing cations), and low concentrations of aqueous organic species], a minimum value of 200 mL/g is a reasonable Cs K_d for use in release and transport analyses. A most reasonable K_d value for Cs in Hanford groundwater contacting Hanford soil is expected to be 500 to 2000 mL/g. For high-salt wastes and acid wastes, a Cs K_d range of <1 to 200 mL/g is recommended, depending on the ionic strength and relative abundances of competing cations. As the relative potassium concentration increases and the overall ionic strength increases, the appropriate Cs K_d value will decrease to the lower part of the range. The available data base indicates that cesium sorption is relatively insensitive to organic constituents. Therefore, at this time no change in the recommended cesium sorption values are proposed as a function of organic constituents present in a given waste stream.

The quality of the cesium K_d data is considered to be good because of the large quantity of data available, which agrees reasonably well, and the wide range of conditions for which data are available.

<u>Strontium</u>

Strontium is the most extensively studied radioisotope in the Hanford Site soil environment. Thermodynamic data summarized by Ames and Rai (1978) indicate that strontium exists as a divalent cation throughout the potential range of groundwater pH in the absence of complexing anions and organic ligands. It is generally accepted that strontium sorbs by ion exchange as a cation. The degree of sorption in Hanford soil is dependent on the types and concentrations of other cations in solution that can compete successfully for sorption sites. A large data base exists that includes measurements of the effects of different cations and their concentrations on strontium sorption. The data indicate that all common cations (e.g., hydrogen, potassium, sodium, calcium, and magnesium) can influence strontium sorption depending on their

concentrations. The experiments done with Hanford Site soil are reviewed below.

To investigate the effect of hydrogen, Rhodes (1957b) measured strontium K_d as a function of pH. Sorption K_d values of 5, 30, and 120 mL/g were observed at pH values of 6, 8, and 10, respectively. McHenry (1958) investigated the effects of varying concentrations of potassium, lithium, sodium, and ammonium. Initial strontium concentrations of 10^{-4} to 10^{-7} M with equal amounts of one or two other cations in solution at approximately neutral pH resulted in a strontium K_d in the range 20 to 80 mL/g. These data indicate that these cations do not compete strongly at these concentrations for sorption sites with strontium. Routson et al. (1981) investigated the effects of a wider range of sodium concentrations (10^{-3} to 3 M) and observed a drop in strontium K_d from 39 to 5.6 to 0.6 mL/g at 1.5×10^{-2} , 1.5×10^{-1} , and 1.5 M sodium, respectively. In the presence of potassium, the Sr K_d dropped from 23 at 1×10^{-2} M to 7.9 at 5×10^{12} M potassium.

Experiments performed to measure the effect of the divalent cations calcium and magnesium on strontium sorption indicate that these cations are the more successful competitors for sorption sites. Rhodes (1956) and Brandt (1957) measured strontium K_d in the range of <1 to 10 mL/g at calcium concentrations between 1 x 10^{-3} and 1 x 10^{-2} M and pH values of 6 to 12. Similarly, Routson et al. (1981) has shown that the strontium K_d drops from 10 to 0.3 mL/g when calcium concentrations increase from 5 x 10^{-3} to 2 x 10^{-1} M. Nelson (1959) found strontium K_d to drop from 19 to 2 mL/g as magnesium concentrations increased from 1 x 10^{-3} to 1 x 10^{-1} M.

The most recent results available were conducted by Serne et al. (1990, 1991). Strontium K_d results range from 23.4 \pm 4.1 mL/g at 5 days to 18.1 \pm 4.0 mL/g at 44 days contact between Trench 8 soil and Hanford groundwater. Results determined for contact between Hanford groundwater and CGS-1 sediment average to 19.1 \pm 2.8 for equilibration times of 4 to 35 days. TBS-1 soil results average to 23 \pm 13 mL/g for the same equilibration periods.

Experimental data indicate that common inorganic anions at concentrations observed in the environment do not form significant complexes with strontium, and subsequently do not form anionic aqueous species that inhibit sorption.

McHenry (1958) measured strontium K_d as a function of nitrate, chloride, oxalate, sulfate, and phosphate at concentrations of $\approx 10^{-7}$ to 1 x 10^{-4} M and neutral pH. Only phosphate and oxalate influenced strontium sorption and only at their highest concentrations. These anions actually enhanced the measured sorption values. Work by Ames et al. (1958) demonstrated that a calcium phospate mineral, apatite, will form in the soil system containing phosphate and calcite. The calcium dissolved from calcite combines with the phosphate to form the apatite. If strontium is available, it will behave similarly to calcium and coprecipitate in the newly formed phosphate mineral. Consequently, the observed increase in strontium "sorption" is probably due to coprecipitation reactions. It is hypothesized that a similar type of reaction occurs with oxalate.

Little quantitative work has been done to measure K_d values of strontium in the presence of organic anions. Work that has been done indicates that a definite interaction between strontium and some organics does occur, which reduces the sorption of strontium. Knoll (1969) showed that a mixture of 0.4 M d-(2-ethylhexyl) phosphoric acid (d-2-EHPA) and 0.2 M tributyl phosphate (TBP) in normal paraffin hydrocarbons (NPH) would completely desorb strontium from a soil column. Ames et al. (1958) indicated that cyanide (CN $^-$) would also complex with strontium. Other experimental data not related to the Hanford soil environment (Fuller and L'Annunziata 1969) show that N-(2-hydroxyethyl) ethylenediaminetetraacetic acid (HEEDTA), ethylenediaminetetraacetic acid (EGTA), and diethylenetriaminepentaacetic acid (DTPA) will form anionic complexes with strontium and reduce sorption.

Given this data base, sorption K_d for strontium in Hanford Site soil will fall between 0 and 100 mL/g, except in the presence of phosphate or oxalate in which case "sorption K_d " are of the order of 200 to 500 mL/g. Strontium sorption is sufficiently sensitive to groundwater cation concentrations and its own initial concentration that narrowing the K_d range is dependent on the individual situation. A conservative value of 5 to 10 mL/g is recommended recognizing that sorption values may be much higher. A probable average value for ambient Hanford conditions is 20 mL/g. The use of low values is based on the unconfined aquifer groundwater compositions, which contain $\approx 10^{-3}$ M of

calcium. Relatively speaking, calcium should be the dominant factor affecting strontium sorption under most conditions in ambient Hanford soil. Under acidic conditions, a recommended sorption range is 3 to 5 mL/g. Given the much higher salt concentrations in single-shell tank wastes, the recommended K_d for Sr in environments dominated by high ionic strength process liquid wastes is 1 mL/g. Limited data on strontium interactions with organic constituents (cyanide, TBP) in Hanford soil suggests that anionic species could form that would further reduce the sorption of strontium.

The quality of the strontium K_d data is considered to be good because of the large quantity of data available, which agrees reasonably well, and the wide range of conditions for which data are available.

Cobalt

Thermodynamic data summarized by Ames and Rai (1978) indicate that aqueous cobalt exists primarily as Co^{2+} up to a pH of approximately 9.5 and then as a neutral hydroxide species $Co(OH)_2^0$ at pH >9. Thermodynamic data also predict that cobalt will complex with common anions (chloride, nitrate, hydroxide, and sulfate) to form mostly neutral or anionic species. These species will not occur at significant concentrations under ambient Hanford groundwater conditions. At a pH value of 9 or less, cobalt should sorb via cation exchange if it does not react with other anions to form anionic or neutral species. Routson et al. (1981) investigated the influence of calcium, sodium, and potassium on cobalt sorption onto a variety of Hanford sediments taken from different boreholes. Of the three cations, calcium was the most successful competitor with cobalt for sorption sites. Sorption $K_{\rm d}$ values for cobalt decreased from 3400 to 200 mL/g as calcium concentrations increased from 2 x 10^{-3} to 2 x 10^{-1} M. On the other hand, cobalt K_d values increased with increasing sodium and potassium concentrations (from 2100 to 4700 mL/g as Na increased from 1 x 10^{-3} to 3 M, and from 500 to 3400 mL/g as potassium increased from 2 x 10^{-3} to 2 x 10^{-1} M). These data clearly indicate that the cation exchange process is not the only process affecting cobalt sorption. The authors suggested that colloid formation and physical sorption were occurring. Conversely, Barney (1978) observed that the sorption of cobalt on Hanford soil was reduced in the presence of potassium. Specific K_d values were not reported.

Some field studies and laboratory studies on Hanford soil indicate that cobalt readily reacts with organic and inorganic anions when they are present at high concentrations. These observations are supported by other studies on soils similar to Hanford soil. Haney (1967) reported the occurrence of cobalt in groundwater under the 216-BY crib. He proposed that the apparent high mobility of cobalt in the soil column was due to the formation of anionic cobalt phosphate complexes resulting from the high phosphate content in the waste stream. Barney (1978) observed that the sorption of cobalt on Hanford soil was reduced in the presence of nitrite (NO_2^-) and humic acid, presumably because of the formation of anionic or neutral complexes with cobalt. Wilding and Rhodes (1963) demonstrated that the addition of EDTA to a soil water system would reduce the cobalt K_d by a factor of 100.

Distribution coefficients have recently been determined for cobalt using Hanford Trench 8 soil (200 W Area) and Hanford groundwater or waste leachate solutions (Serne et al., 1991). The results were essentially the same for equilibration periods of 5 days or 43 days. The average K_d value determined for Trench 8 soil and Hanford groundwater was 1.2 x 10^4 mL/g. K_g values were also determined for Trench 8 soil and leachate solutions representative of solution percolating through buried solid waste at Hanford. An average K value of 54 mL/g was determined between Trench 8 soil and leachate solution derived from Hanford groundwater in contact with wood, cardboard and paper. This value is significantly lower than that determined using unaltered groundwater. This is probably due to complexation of the cobalt in solution by organic acids leached from the waste materials (the leachate in these experiments contained between 407 and 480 ppm total organic carbon). In a third set of experiments, adsorption of cobalt was determined between Trench 8 soil and a leachate solution derived from Hanford groundwater in contact with a wider variety of wastes including wood, cardboard, paper, plastic, rubber, nylon, cotton, cloth, canvas, various tapes and cement. The average K_d value determined in this set of experiments was 16 mL/g. This value is even lower than the previous set of experiments despite the much higher pH of the solution (pH = 12.1) caused by the cement. This is probably due to the increased deprotonation of organic acids leached from the wastes, causing a greater degree of complexation.

Based on the foregoing information, the recommended range of sorption K_d values for cobalt is 2 x 10^3 to 1.2×10^4 mL/g for ambient Hanford soil conditions (neutral to slightly basic pH, low ionic strength, and low organic content). A range of K_d values for cobalt between Hanford soil and leachates percolating through Hanford solid wastes is 10 to 50 mL/g. A recommended range for high-salt, high-organic, and/or acid conditions cannot be specified with any confidence because of the lack of data. General indications are that K_d values will be much lower than ambient condition values.

The quality of the cobalt K_d data is considered to be good because of the large quantity of data available, which agrees reasonably well, and the wide range of conditions for which data are available.

Bismuth

No adsorption data is available for bismuth adsorption onto Hanford soils. The only one study was found in which bismuth adsorption onto soils was studied (Gerritse et al., 1982). In this study it was found that adsorption of bismuth onto soils was high. K_d values ranged from 500-1000 mL/g for a sandy top soil in contact with inorganic solutions at pH values that ranged from 5.2 to 7.7; for a sandy loam in contact with the same solutions, the K_d values ranged from 5000 to 19,000 mL/g. Under ambient Hanford groundwater conditions bismuth will exist as the Bi(OH) $_3$ (aq) species and will have a solubility of approximately 4 x 10⁻⁴ M (Baes and Mesmer, 1976). Because bismuth will exist as the Bi(OH) $_3$ (aq) species both in the experimental solutions of Gerritse et al. (1982) and in Hanford groundwaters it is expected that adsorption of bismuth onto soil will also be strong. Due to the uncertainty in the adsorption behavior of bismuth; however, it is recommended that laboratory adsorption studies be conducted for bismuth in Hanford groundwater onto Hanford soil.

<u>Uranium</u>

Under oxidizing conditions (typical for Hanford vadose zone sediments and the upper unconfined aquifer), dissolved uranium is predicted to exist as a cation (UO_2^{2+}) up to a pH of approximately 6, as a neutral hydroxide species $\mathrm{UO}_2(\mathrm{OH})_2^0$ from a pH of approximately 6 to 8, and as an anionic carbonate $\mathrm{UO}_2(\mathrm{CO}_3)_3^{4-}$ above a pH value of 8. Uranium may also complex with other anions

(e.g., fluoride, chloride, and phosphate) to form neutral or anionic species, but such complexes should not exist in significant concentrations under ambient Hanford groundwater conditions. These estimated species distributions suggest that uranium would sorb via cation exchange under acid conditions and sorb very poorly under neutral and basic conditions.

Recent laboratory studies indicate that uranium sorption onto Hanford soil is weak under ambient Hanford groundwater conditions (Serne et al., 1990, 1991). K_d values determined for uranium using Trench 8 soil and Hanford groundwater are as follows: 1.9 ± 1.4 mL/g at 5 days and 2.1 ± 0.6 mL/g at 44 days of contact (Serne et al., 1991). Adsorption of uranium onto Hanford Trench 8 sediment from solid waste (wood and paper) leachates containing significant concentrations of organic matter was significantly decreased over that of ambient groundwater. The average K_d under these conditions value was essentially zero. K_d values determined between Trench 8 sediment and leachate from solid waste containing a variety of organic materials and cement (high pH and relatively high ionic strength) were determined to be 2850 ± 960 mL/g after 5 days and 320 ± 140 after 44 days of contact. In another study (Serne et al., 1990), the average K_d for uranium was determined to be 1.7 ± 4.2 mL/g for Hanford groundwater and CGS-1 sediment and 79 ± 26 mL/g for TBS-1 sediment.

Characterization of 300 Area soil underneath the 316-4 crib by Ames and Phillips (1979) indicates that uranium is rather immobile because of solubility constraints rather than sorption. Strong evidence is presented that a uranium phosphate has precipitated because of the high phosphate content in the waste stream. Leaching experiments were completed as part of the study and showed that 0.1 N HNO₃ acid was very successful at removing uranium from the contaminated soil column while distilled water and a methyl isobutyl ketone solution did not remove uranium from the soil. The data indicate that nitric acid dissolves the uranium phosphate phase. In some recent preliminary work² using unsaturated columns, retardation factors were determined for uranium using Hanford Trench 8 soil and groundwater under

²1991 unpublished results. WSU-Tri Cities, Richland, Washington.

unsaturated conditions. An R of 2.3 was determined at 77% and 26% saturation. This corresponds to a $\rm K_d$ of 0.3 mL/g.

General indications are that uranium sorption values will be low under most ambient Hanford circumstances because uranium tends to form neutral or anionic carbonate species at neutral or basic pH values. A range in $K_{\rm d}$ of 0.3 to two is recommended for uranium under ambient Hanford groundwater conditions.

- The quality of the uranium $\,K_d$ data is considered to be fairly good. Fewer data are available for uranium than Cs, Sr, or Co, but the agreement among the data is reasonably good. Data are not available for acidic solutions containing organic complexants.

Plutonium

A moderate number of investigations of plutonium behavior in Hanford Site soil have been completed. Thermodynamic data summarized by Ames and Rai (1978) indicate that plutonium may form anionic or cationic aqueous species depending on solution pH and Eh. For oxidizing conditions expected at the Hanford Site, cationic plutonium species should predominate up to a pH value of approximately 6 while plutonium carbonate and plutonium hydroxyl-carbonate complexes with negative charges are expected to occur in the pH range of 6 to 12. The potential for plutonium sorption should, therefore, decrease with increasing pH. Evidence exists (Rhodes 1957c), however, that plutonium tends to hydrolyze above a pH value of 2. Hydrolysis leads to the formation of finely dispersed precipitates, which can be removed from solution by physical sorption processes and reduce plutonium mobility.

Plutonium sorption has been investigated as a function of pH, salt content, and organic complexants. Rhodes (1957c) showed that plutonium sorption onto Hanford soils is very sensitive to pH. Minimum Pu sorption occurs in the pH range of $\approx \!\! 1$ to 3 (K_d of $\approx \!\! 30$ mL/g). Maximum Pu sorption occurs in the pH range of $\approx \!\! 4$ to 8.5 (K_d, >1980 mL/g) and moderate Pu sorption occurs in the pH range of $\approx \!\! 10$ to 12 (K_d, 80 to 380 mL/g). It is likely that physical sorption of precipitates is a significant process in the maximum sorption range. Limited investigation of cation competition effects on plutonium sorption indicates negligible competition in the neutral pH range.

Rhodes (1957c) measured a Pu $\rm K_d$ of 275 in a 4 M solution of sodium nitrate at pH of \approx 7. He also indicated negligible effects on sorption in the presence of 4 M ammonium. Cation exchange competition may influence plutonium sorption at extremely acid pH conditions. Hajek and Knoll (1966) measured $\rm K_d$ values of <1 mL/g at pH values of \approx 1 to 3 and combined calcium, sodium, and magnesium concentrations of \approx 2.5 M. An alternate explanation of Hajek and Knoll's data would be that Pu precipitation is minimized at low pH values and thus the apparent $\rm K_d$ is small.

Investigation of the effects of inorganic anions on plutonium sorption has been limited to nitrate. Evidence indicates that nitrate has little effect on plutonium sorption (Rhodes 1957b). Numerous organic anions have been shown to react with plutonium, forming soluble organic complexes that reduce the sorption of plutonium; these include DBBP, TBP, d-2-EHPA, and hydroxyacetic acid (Knoll 1969). The data show that different plutonium mobilities result from the order in which plutonium and the organics are introduced to a soil column. The least influence occurs when plutonium is first sorbed onto the soil column without organics, followed by flushing of the column with organic constituents. The greatest reduction in sorption occurs when plutonium and the organic complexants are both present in the infiltrating solution. The data are insufficient to predict $K_{\rm d}$ values for plutonium in the presence of these species.

It should be noted that the oxidation state of Pu was not characterized in the work discussed above. Several oxidation states of Pu can co-exist in groundwaters. Under oxidizing conditions, the most likely oxidation states of Pu in the above experiments (as well as Hanford groundwater) is $PuO_2^+ > PuO_2^{2+} > Pu^{4+} > Pu^{3+}$.

Based on the available data, the recommended range of K_d values for plutonium under ambient Hanford soil conditions is ≈ 100 to 1000 mL/g. Under acid conditions (pH of ≈ 1 to 3), the recommended Pu sorption K_d is < 1 mL/g. A wide range of Pu K_d values is possible in neutral to basic pH systems containing appreciable organic compounds, and further data must be collected before a reasonable range can be recommended.

The quality of the plutonium K_d data is considered to be fair. Much of the work failed to separate precipitation effects from adsorption effects and the oxidation state of plutonium was not characterized. Fewer data are available for plutonium than for many of the contaminants reviewed here and the variability caused by changes in chemical factors is not well documented. On the other hand, it is known from the general literature that plutonium is quite immobile in most ambient groundwater environments. Further work to determine the adsorption properties of plutonium onto Hanford soils should be considered.

Technetium

Experimental work on soils similar to those at Hanford indicate that technetium exists as a negative anion TcO_4^- in oxidizing soil environments and does not readily complex with other chemical species. Consequently, technetium is considered to be relatively nonadsorbing in almost every oxidizing soil environment. Routson et al. (1976) measured technetium sorption on Hanford soil and measured K_d values which ranged from 0 to < 1 mL/g; recent results by Serne et al. (1990, 1991) are very similar. Technetium K_d values determined with Trench 8 soil and Hanford groundwater were -0.1 \pm 0.2 mL/g at 5 days and 0.2 \pm 0.7 mL/g at 44 days (Serne et al., 1991). Average technetium K_d values determined for Hanford CGS-1 soil and Hanford groundwater were 0.1 \pm 0.7 mL/g, and 0.1 \pm 0.5 mL/g for TBS-1 soil (Serne et al., 1990). K_d values determined with Hanford sediment (Trench 8) and leachates derived from Hanford groundwater and solid waste (wood, cardboard and paper), which contained considerable concentrations of total organic carbon (407 to 440 mg C/l), showed no significant difference from those determined without organics present. Significant sorption may occur in soils that contain considerable organic matter, which tends to sorb anionic species and may reduce technetium to its +4 valence state causing precipitation or sorption. Because these types of soils are nonexistent at the Hanford Site, the recommended sorption K_d range for Tc for all types of waste conditions is 0 to <1 mL/g.

The quality of the technetium K_d data is considered to be very good as a result of the good agreement between the several Hanford-specific studies and the studies published in the general literature.

Cyanide

Hydrogen cyanide is a weak acid with a pK of 9.2. Cyanide in Hanford groundwater will therefore exist largely as an uncharged species. Sitespecific adsorption data onto Hanford soils are not available; however, hydrogen cyanide adsorption onto soils is expected to be minimal. Data from Alesii and Fuller (1976) suggest that K_d values for cyanide range from 0.1 to 1.0 for various soils.

Although cyanide adsorption is expected to be minimal actual data for Hanford conditions are nonexistent, and the affects of different chemical conditions are not known. Thus it might be useful to perform some Hanford-specific adsorption experiments once the chemical environments of interest are defined.

Phosphate

Phosphate adsorption data for Hanford soils are not available. Data determined for a variety of other soils (Goldberg and Sposito, 1984) indicate that K_d values for most soils should exceed 5 mL/g. Estimating a reliable K_d value for Hanford soil is difficult due to the large number of factors which can significantly influence its value. These factors include the concentration of calcium carbonate and iron and aluminum oxides in the soil, and chemical composition of the groundwater, especially the concentration of dissolved calcium, ionic strength and pH.

Although adsorption of phosphate onto soils is likely to be an important attenuation mechanism in soils and groundwaters, the solubility of phosphate will be a very important factor limiting its dissolved concentration, particularly near the source. Using the MINTEQ geochemical code and analytical composition data for a typical Hanford groundwater, it is estimated that the total phosphate solubility will be approximately 2 x 10^{-8} M (\approx 2 μ g/L), (assuming equilibrium with hydroxyapatite). This concentration will be further diminished by adsorption onto soil.

Pore waters in Hanford vadose and upper unconfined aquifer sediments rarely show measurable concentrations of dissolved phosphate (Serne et al.,

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1990), which corroborates the possibility that solubility of hydroxyapatite controls phosphate concentrations. It is inappropriate to describe solubility controlled contaminants using K_d values, although this is often done for simple transport calculations. To satisfy transport modelers who require K_d values as the only way to describe mobility, phosphate should be considered quite immobile under ambient Hanford conditions and under high ionic strength alkaline conditions. We approximate the mobility phosphate with a K_d value of 50 mL/g. The quality of this value must be considered purely as an educated guess. Phosphate mobility increases under acidic conditions as a result of the increased solubility of hydroxyapatite with decreasing pH.

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Change Number	APPROVED DOCUMENT CHANGE CONTROL FORM	Date	
22	Do not use blue ink. Type, or print in black	4/23/92	
Document Number & RI/FS Work Plan : Operable Unit, Hawashington		ed	•
Originator M. A. Buckmaster	H23/92 Phone , 200-BP-1 RI Coord. 376-1792		
Description of Change Modify Task 2 so boreholes locate background conce	urce sampling throughout the text to indica d in the 600 Area will not be required to d	te that (3) letermine	•
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Per Action Plan for Implementation of the Hanford Consent Order and Compliance Agreement, Section 9.3

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- 1. Sr90 to 100 years for crib B-43: Kd=10m1/g & Kd=1m1/g
- 2. Cs137 to 100 years for crib B-43: Kd=200ml/g & sludge layer with 2000 ml/g
- 3) Sample selection for physical property testing
- 4) Sensitivity analyses

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- 5) Incorporation of new lab data as it becomes available
- 6) Interact with regulators on details
- 7) Selection of contaminants of interest

200-BP-1 TASK 6 ACTIVITIES

Task 6 Phase IB wells:

o Well 699-57-59 is completed and sampled.

Well Remediation:

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- o Wells 699-59-58 and 699-60-57 are completed.
- o Well 699-60-60 Surface seal completed and piezometer removed. Removal of concrete plug remains.
- o Begin installation of 200 Area posts and pads.

200-BP-1 SORPTION/COLUMN LEACH TESTING

Column Leach Testing:

- o Testing has been completed for 216-B-57 and 216-B-49.
- o Testing is currently underway for crib samples 216-B-43.

Sorption Testing:

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- o Literature Search
- o Testing Methodology:
 - o Groundwater from 699-50-53A will be used.
 - o 5 tracer tests will be performed using CN/C-14, Cs-137/Sr-90, Tc-99, Co-60, and Pu.
 - o Currently revising the test plan with testing tentatively scheduled for next month.

200-BP-1 SAMPLE VALIDATION SUMMARY

CHEMICAL SAMPLES													
Sample Type	Total Samples	Number of Samples Received from Laboratory	Total Validated Samples	Total Unvalidated Samples	Total Samples which have Partial Data Validated								
2nd Quarter Groundwater	190	190	117	73	10								
3rd Quarter Groundwater	135	135	120	15	0								
4th Quarter Groundwater	110	0	0	0	0								
Crib Samples to Date	321	131	7	277	9								

		RADIOCHEM	ICAL SAMPLES		
Sample Type	Total Samples	Number of Samples Received from Laboratory	Total Validated Samples	Total Unvalidated Samples	Total Samples which have Partial Data Validated
2nd Quarter Groundwater	60	60	0	0 .	0
3rd Quarter Groundwater	52	52	0	0	0
4th Quarter Groundwater	56	12	0	0	0
Crib Samples to Date	141	29	0	0	0

SOURCE AND VADOSE SAMPLING

- o Source and Vadose Sampling has been completed.
- o 28 boreholes were drilled. Maximum contamination encountered 12,000 mRad/hr and 1500 mRad/hr.
- o 3 boreholes in Crib 216-B-47 remain to be abandoned.
- o Cleanup activities will continue for 4-6 weeks.

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PHASE I REMEDIAL INVESTIGATION TASK-1 MANAGEMENT & STATUS REPORTS

TASK-2 SOURCE SAMPLING AND ANALYSIS

TASK-2a PREPARATION

TASK-2b DRILLING AND SOIL SAMPLING

TASK-2c SAMPLE HANDLING AND TRANSFER

TASK-2d LABORITORY AVAIL. & CHEMICAL ANALYSIS

TASK-2e BOREHOLE GEOPHYSICS

TASK-2f GEODETIC SURVEY

TASK-2d BOREHOLE ABANDONMENT

TASK-3 SURFACE/NEAR SURFACE SOIL SAMPLE/ANALYSIS

TASK-3a PREPARATION

TASK-3b EVALUATE & TEST LEAK DETECTION TECHNIQUE

TASK-3c SCINTILLATION SURVEY OF LAND SURFACE

TASK-3d STAGE 1 SOIL PROBE SURVEY

TASK-3e STAGE 2 SOIL PROBE SURVEY

TASK-3f SOIL SAMPLING

TASK-3g GEODETIC CONTROL & SURVEY

TASK-3h LABORATORY AVAIL. & CHEMICAL ANALYSIS

TASK-4 VADOSE ZONE SOIL SAMPLING & ANALYSIS

TASK-4a REVIEW & PREPARATION

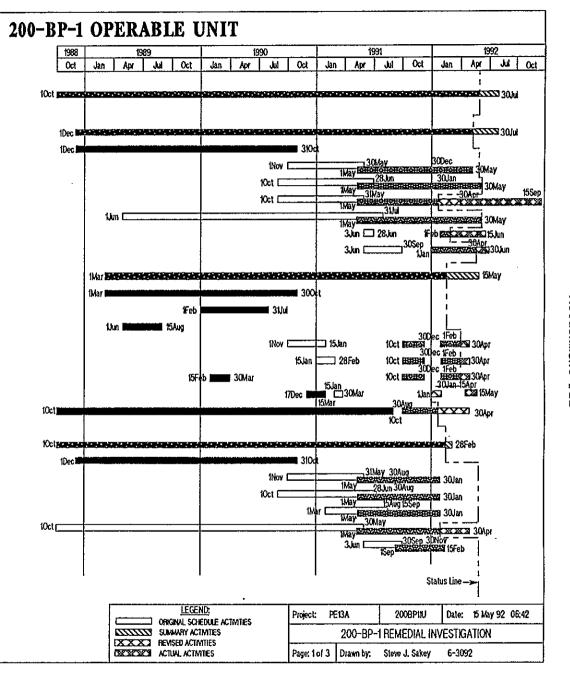
TASK-4b DRILLING & SAMPLING

TASK-4c SAMPLING, HANDLING & TRANSFER

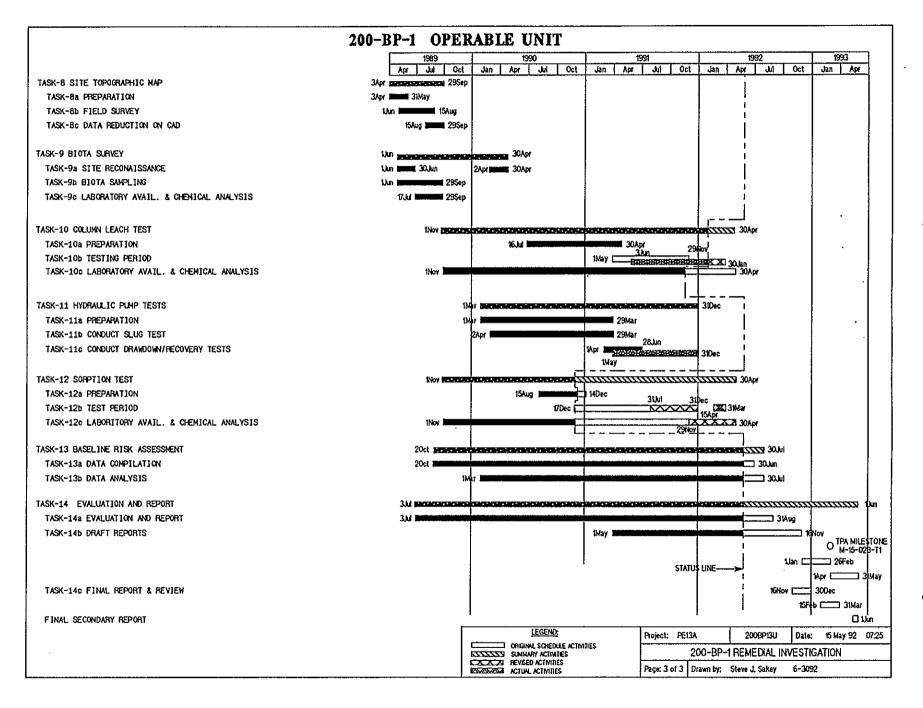
TASK-4d BOREHOLE GEOPHYSICS

TASK-4e LABORATORY AVAIL. & CHEMICAL ANALYSIS

TASK-4f BOREHOLE ABANDONMENT



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12/Page 3 of 3

Distribution

Unit Manager's Meeting: 200-BP-1 Operable Unit May 28, 1992

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ADMINISTRATIVE RECORD: 200-BP-1; Care of EDMC, WHC (H4-22)

This list has been updated. Please inform Suzanne Clarke (SWEC) of deletions or additions to the distribution list.